

Corrosion of Carbon Steel in Hybrid N-Methyl-2-Pyrrolidone - Monoethanolamine Solutions for Carbon Dioxide Absorption Unit Application

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Abstract. Corrosion is defined as degradation or deterioration of material and its properties interact with environment by electrochemical and chemical reaction. It not only causes monetary loss but also potential issues for human health. This study investigates the corrosion rate of carbon steel when immersed in hybrid n-methyl-2-pyrrolidone (NMP) - monoethanolamine (MEA) solutions in comparison with immersion in the conventional aqueous MEA solution. ASTM G31 was adopted in research design methodology and the corrosion rate was evaluated via mass loss measurement. The corrosion rate of carbon steel at 35 days was lowered by approximately 14% when NMP partially replaced the water in the MEA solution. Meanwhile, the corrosion rate was lowered by approximately 20% when NMP fully replaced the water in the MEA solution. Therefore, the corrosion of carbon steel in MEA solution was found to be reduced when NMP partially or fully replaced the composition of water.

1. Introduction

Corrosion is a phenomenon that is intrinsic to every matter in nature. All the natural processes have tendency to achieve its lowest energy states, where pure metals will revert to their lowest energy state as oxides or sulphides [1]. Corrosion occurs in form of general, galvanic, pitting, crevice, intergranular, erosion, selective leaching and stress corrosion cracking. It is very important to study corrosion because corrosion can lead to equipment failure and harmful or more severe effect. In this 21st century, none of enterprise or organization should tolerate the major failure of corrosion; especially those may involve injuries, fatalities and shutdown of system as well as severe environment contamination [1].

Corrosion issues also virtually lead to huge amount of expenditure to process cost. According to NACE International [1] the plant expenditure due to corrosion was estimated about \$47.9 billions for utilities and \$17.6 billion for production and manufacturing of the maintenance cost related.



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Kohl and Nielsen [2] highlighted that all amine-treating plants for chemical absorption experienced corrosion problems due to the process temperature, amine concentration as well as dissolved carbon dioxide or some degradation products. MEA is commonly used in amine-based absorption process due to its high reactivity. Kladkaew et al. [3] found that addition of corrosion inhibitor in MEA based solution could reduce the effectively reduce the corrosion rate. However, the additional corrosion inhibitor would contribute to increase of cost. Meanwhile, Veawab et al. [4] highlighted that NaVO_3 inhibitor provided 96% inhibition efficiency without pitting tendency. Nevertheless, it only worked under limited operating condition.

Carbon steel is widely used in construction of equipment and piping in amine treating plants [5]. Carbon steel is an alloy of carbon and iron, carbon content up to maximum 1.5-2.0% [6]. The carbon is presence in form of iron carbide due to its ability to increase the strength and hardness of steel at minimal cost, thereby making carbon steel column most common equipment for CO_2 capture in industries [7].

Tan et al. [8] found that NMP, a physical organic solvent in MEA solution, was effective for CO_2 absorption in high pressure condition. However, the corrosion behaviour of the MEA hybrid solution towards carbon steel is still not clearly understood. As such, this work aims to investigates the corrosion rate of carbon steel coupons immersed in aqueous MEA solution and MEA hybrid solutions containing NMP either as partial or full replacement of water.

2. Materials and Methods

2.1. Materials

Monoethanolamine, MEA (purity: 99.9%); and N-Methyl-2-pyrrolidone, NMP (purity: 99.98%), used in this research were purchased from Merck.

2.2. Methods

The experiments setup was modified and carried out in accordance with ASTM G31[9]. This procedure is a standard method for laboratory immersion corrosion testing of metals. The coupons for corrosion test for this study were carbon steel C1018 (Metal Samples, USA). Their chemical compositions are C – 0.75-0.88; Fe – 98.0-99.0; Mn – 0.60-0.90; S – 0.05 (max) & P – 0.04. All the specimens were cleaned using distilled water to remove dirt. The specimens were then dried with lint free tissue.

Three categories of amine solution were prepared: a) MEA (20wt%) + water (H_2O) (80wt%), b) MEA (20wt%) + H_2O (40wt%) + NMP (40wt%) and c) MEA (20wt%) + NMP (80wt%). The carbon steels were immersed in solution for a period of 7, 14, 21, 28 and 35 days. When the testing period ended, each coupon was rinsed with forceful stream of tap water, followed by rinsing with distilled water and scrubbing with clean scouring pads until loose product on the carbon steel was removed. The mass of coupon before and after the immersion periods were recorded accordingly. The corrosion rate of carbon steel coupons was the evaluated by using the equation (1) based on mass loss determination as follows:

$$\text{Corrosion Rate (MPY)} = \left(\frac{M_0 - M_e}{A \times T \times \rho} \right) \times K \quad (1)$$

where

$M_0 - M_e$ = Difference in mass (grams);

K = Constant (section 8.1.2 ASTM);

A = Area (cm^2);

T = Time (hours);

ρ = Density of metals (g/cm^3)

Each set of the experiment was conducted in duplicate and the average results are reported in this paper. The immersed carbon steel coupons were further analysed using scanning electron microscopy (SEM)

(Hitachi, TM3030 Tabletop Microscope) to observe the morphology of the surface after immersion in solution for 35 days.

3. Result and Discussion

Figure 1 and Figure 2 shows the mass loss of carbon steel and the corrosion rate over 7 days of interval period until 35 days of immersion. It was observed that the corrosion rate increased with the interval time. This is because the coupons had sufficient time for the corrosion activity to evolve on the surface of the steel with longer period of immersion. Carbon steel coupon immersed in MEA + H₂O solution experienced the highest mass loss and corrosion rate of 2.48% and 2.97MPY. Carbon steel coupon immersed in MEA+NMP+H₂O solution had 2.12% of mass loss and 2.54MPY of corrosion rate after 35 days. Meanwhile, the carbon steel coupon, which was immersed in solution containing MEA + NMP solution had the lowest mass loss of 1.98% and corrosion rate of 2.37MPY after 35 days. The results indicated that the corrosion rate was lowered by approximately 14% when NMP partially replaced the water in the MEA solution. On the other hand, the corrosion rate was lowered by approximately 20% when NMP fully replaced the water in the MEA solution. The sequence of highest percentage of mass loss and corrosion rate was found to be in the following order: MEA+H₂O>MEA+NMP+H₂O>MEA+NMP.

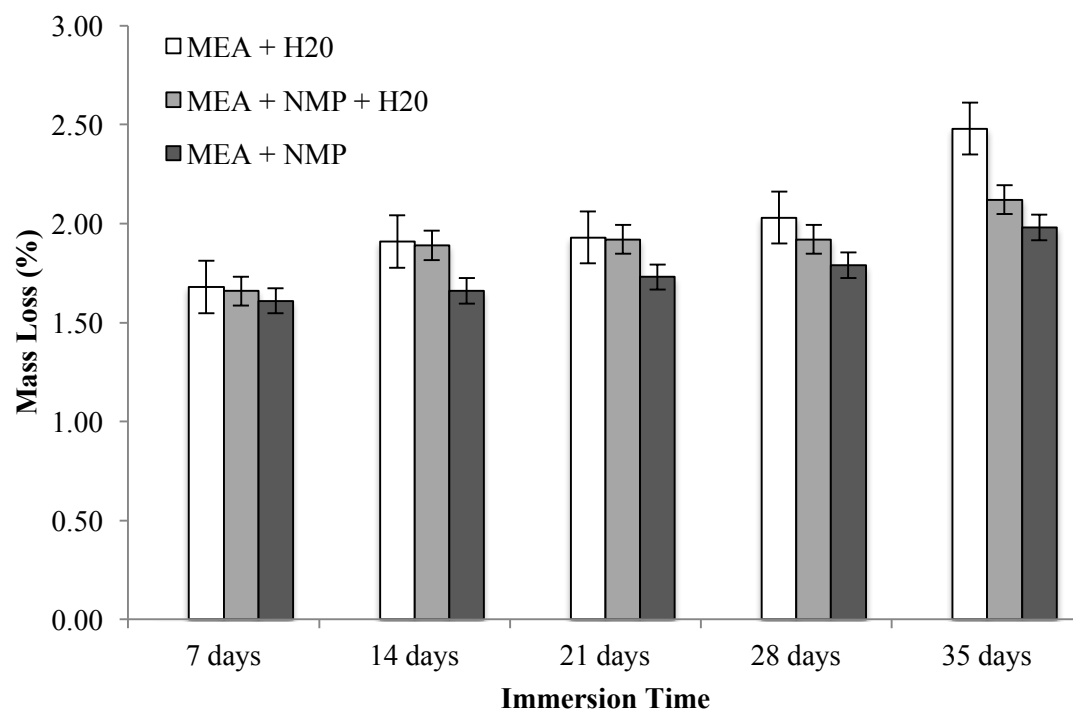


Figure 1. Plot of mass loss versus immersion time for carbon steel.

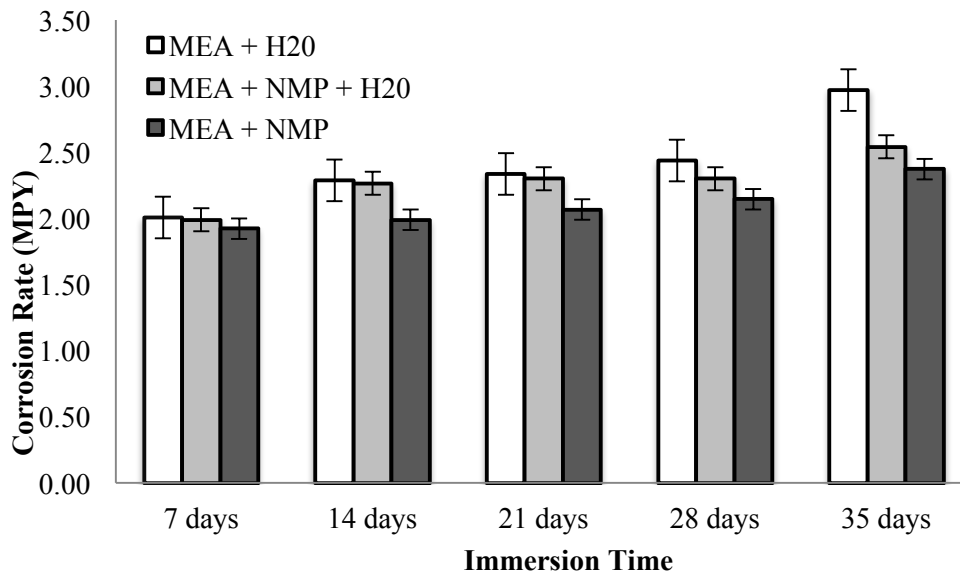


Figure 2. Plot of corrosion rate versus immersion time for carbon steel.

Figure 3 shows the morphologies of carbon steel coupons that were immersed in three types of MEA solution respectively. Figure 3 (a) and (b) show SEM image of the carbon steel surface, which was immersed in MEA + H₂O. Based on the image, some bubbles formation was observed to occur. According to Wu et al. [10], these bubbles could be hydrogen bubbles, which were recognized as features of carbon steel in beginning of pitting corrosion. On the contrary, Figure 3 (c) and (d) which show carbon steel surface immersed in MEA + NMP + H₂O and MEA + NMP, respectively, had no significant trace of hydrogen bubbles formations. MEA could react with steel in the presence of oxygen and form Iron (III) oxyhydroxide (FeOOH) as the degradation product. However, NMP was deduced not to react with the carbon steel since NMP behaved as organic molecules [11].

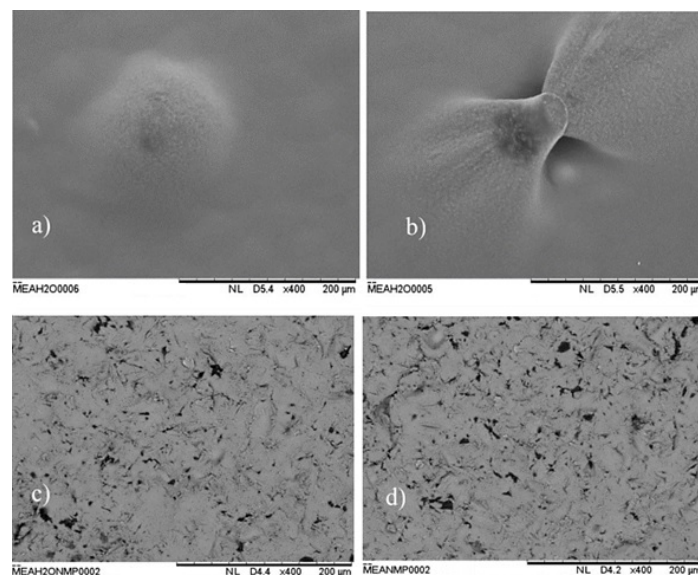


Figure 3. Scanning electron microscopy (SEM) image of surface of carbon steel coupon; (a) & (b) immersed in MEA aqueous solution; (c) immersed in MEA + NMP + H₂O solution; (d) immersed in MEA + NMP solution.

Since the carbon steel coupon that was immersed in MEA aqueous solution had the highest mass loss among others, its high corrosion potential could be due to the compounded reaction between MEA and water with steel. The three main products which could be produced from the reaction mechanisms are $\text{Fe}(\text{OH})_2$, FeOOH and compound of iron oxide hydrate, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Evan [12] reported that the Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$ are considered as rusts but FeOOH was considered as protective layer that will stop the corrosion. However, since it was slightly soluble in water, the film may deteriorate due to defects by dissolution thus only able to provide temporary protection.

For the interval-testing period of a total of 35 days, there was no significant trace of rust that could be seen through naked eyes for all specimens. However, analyzing the different coupon steels via SEM found bubble formation on the steel coupon that was immersed in MEA aqueous solution. Based on the circumstance, it is deduced that certain precursory reaction like oxidation and reduction were taking place as well as to evolve for corrosion thereafter.

4. Conclusion

The mass loss and corrosion rate of immersion carbon steel in three types of MEA solution were studied. It was found that the immersion time had proportional relationship with the mass loss and corrosion rate. The sequence mass loss and corrosion rate after 35 days of immersion was found to be in the following order: $\text{MEA} + \text{H}_2\text{O} > \text{MEA} + \text{NMP} + \text{H}_2\text{O} > \text{MEA} + \text{NMP}$. The corrosion rate of carbon steel at 35 days was lowered by approximately 14% when NMP partially replaced the water in the MEA solution. Meanwhile, the corrosion rate was lowered by approximately 20% when NMP fully replaced the water in the MEA solution. Therefore, the corrosion of carbon steel in MEA solution was found to be reduced when NMP partially or fully replaced the composition of water.

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